Synthesis of the (Dialkylamino)borate, $[Ph_2B(CH_2NMe_2)_2]$, Affords Access to N-chelated Rhodium(I) Zwitterions

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Supporting Information

Experimental Section

All manipulations were carried out in the absence of water and dioxygen using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Acetonitrile, tetrahydrofuran, diethyl ether, dichloromethane, toluene, benzene, and petroleum ether were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Ethanol was distilled under vacuum after stirring over NaOEt for 24h. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. $\{(NBD)RhCl\}_2$ and $\{(CO)_2RhCl\}_2$ were purchased from Strem Chemicals and used without any further purification. Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz, Joel 400 MHz, and Anova 500 MHz spectrometers, unless otherwise noted. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR, ^{11}B NMR, and ^{19}F NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4, neat $BF_3{\cdot}Et_2O$, and neat $CFCl_3$ respectively. IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. MS data for samples were obtained by injection of a hydrocarbon solution into a Hewlett Packard 1100MSD Mass Spectrometer (ES^+) or an Agilent 5973 Mass Selective Detector (EI). Deuterated solvents were degassed and dried over activated 3-Å molecular sieves prior to use.

$(CH_3)_2N(BH_3)CH_2Li{\cdot}(THF)$, 1: In a 200 mL round bottom flask, a solution of 1.6 M *n*-butyllithium in hexanes (85.7 mL, 0.137 mol) was added portion-wise to a stirring solution of $H_3B{\cdot}NMe_3$ (10g, 0.137mol) dissolved in THF (20 mL) at room temperature. Addition was complete after 5 min and the solution was allowed to stir for 5 h. Concentration of the reaction solution in vacuo to 50 mL resulted in precipitation of **1**. The reaction solution was decanted from the solid product, which was then washed with petroleum ether (3 x 40 mL), and dried in vacuo affording spectroscopically pure **1**, (9.2 g, 44%). The mother liquor was concentrated to further yield a second crop of **1** (3.2 g). The total isolated yield was 12.4 g (60 %). ^1H NMR (C_6D_6, 300 MHz): δ 3.55 (m, 4H, (*THF*), 2.68 (s, 6H, (Li-$CH_2N(CH_3)_2$)), 2.01 (bs, 2H, (Li-$CH_2N(CH_3)_2$)), 1.30 (m, 4H, (*THF*). ^{13}C $\{^1H\}$ NMR (C_6D_6, 75.409 MHz): δ 69 (Li-$CH_2N(CH_3)_2$, 67 (*THF*), 60.2 (Li-$CH_2N(CH_3)_2$), 26 (*THF*). $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ -10.16.

$[Ph_2B(CH_2N(BH_3)(CH_3)_2)_2][Li(TMEDA)_2]$, [2][Li(TMEDA)$_2$]: A solution of Ph_2BCl (268 mg, 1.3 mmol) in toluene (5 mL) was added dropwise to $(CH_3)_2N(BH_3)CH_2Li{\cdot}(THF)$ (405 mg, 2.6 mmol) in toluene (6 mL) at room temperature. The addition was complete after 5 minutes and the reaction was stirred for an additional 6 h. Removal of the volatiles in vacuo afforded an oily residue. The oily residue was taken up in 5 mL Et_2O and filtered through Celite to remove LiCl. Upon the addition of TMEDA (350 mg, 3 mmol), [**2**][Li(TMEDA)$_2$] precipitated from the ether solution as a white solid. The solid was isolated via filtration on a sintered glass frit, washed with petroleum ether (3 x 10 mL), and dried in vacuo affording analytically pure [**2**][Li(TMEDA)$_2$], (510 mg, 69%). X-ray quality crystals were grown via petroleum ether diffusion into a benzene solution. ^1H NMR (C_6D_6, 300 MHz, 25°C): δ 8.18 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *ortho*-$B(C_6H_5)_2$), 7.44 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-$B(C_6H_5)_2$), 7.26 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-$B(C_6H_5)_2$), 3.27 (m, 4H, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$, 2.33 (s, 12H, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$), 1.95 (bs, 34H, TMEDA-Li). ^{13}C $\{^1H\}$ NMR (C_6D_6, 75.409 MHz): δ 162 (b, *ipso*-$(B(C_6H_5)_2)$, 136 (s, *ortho*-$(B(C_6H_5)_2)$, 128 (s, *meta*-$(B(C_6H_5)_2)$, 124 (s, *para*-$(B(C_6H_5)_2)$, 72 (b, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$, 58 (s, $(CH_3)_2N(CH_2)_2)$, 53 (s, $(CH_3)_2N(CH_2)_2)$, 47 (s, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$. ^{11}B $\{^1H\}$ NMR (C_6D_6, 128.3 MHz): δ -7.8 (BH_3), -13.9 (Ph_2BR_2). ES-MS (Electrospray): calcd for $C_{18}H_{32}B_3N_2$ $(M)^-$ m/z 309, found $(M+H)^-$ m/z 309, 295 (M-BH_3). Anal. Calcd for $C_{30}H_{64}B_3LiN_6$: C, 65.72; H, 11.77; N, 15.33. Found: C, 65.38; H, 11.69; N, 15.08.

$[Ph_2B(CH_2N(BH_3)(CH_3)_2)_2][NEt_4]$, [2][$NEt_4$]: NEt_4Br (21 mg, 0.1 mmol) in ethanol (0.5 mL) was added to a solution of **2**[Li(TMEDA)$_2$] (218 mg, 0.091 mmol) in 1 mL of ethanol. Solid [**2**][NEt_4] precipitated from the solution as a crystalline solid. The remaining solution was decanted and the crystals washed with ethanol (2 x 1 mL) and petroleum ether (2 x 1 mL). The solids were dried in vacuo to afford analytically pure material (154.7 mg, 88.6%). ^1H NMR (acetone-d_6, 300 MHz): δ 7.64 (d, $^3J_{H-H}$ = 7.5 Hz, 4H, *ortho*-$B(C_6H_5)_2$), 7.08 (t, $^3J_{H-H}$ = 7.5 Hz, 4H, *meta*-$B(C_6H_5)_2$), 6.92 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, *para*-$B(C_6H_5)_2$), 3.46 (q, $^3J_{H-H}$ = 7.2 Hz, 8H, $N(CH_2CH_3)_4$), 2.78 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$), 1.96 (s, 12H, $Ph_2B(CH_2N(BH_3)(CH_3)_2)$), 1.38 (tt, $^3J_{H-H}$ = 2.1, 7.2 Hz, 12 H, $N(CH_2CH_3)_4$). ^{13}C $\{^1H\}$ NMR (acetone-d_6,

125.7 MHz): δ 158 (q, *ipso*-B(C_6H_5)$_2$), 136 (s, *ortho*-B(C_6H_5)$_2$), 127 (s, *meta*-B(C_6H_5)$_2$), 124 (s, *para*-B(C_6H_5)$_2$), 69.8 (q, $^1J_{B-C}$ = 43.2 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 66 (bs, $N(CH_2CH_3)_4$), 47.7 (s, $Ph_2B(CH_2N(CH_3)_2)$, 24 (s, $N(CH_2CH_3)_4$). ^{11}B {^1H} NMR (acetone-d_6, 128.3 MHz): δ -5.1 (BH_3), -14 (Ph_2BR_2). ES-MS (Electrospray): calcd for $C_{18}H_{32}B_3N_2$ $(M)^-$ m/z 309, found $(M+H)^-$ m/z 309, 295 (M-BH_3). Anal. Calcd for $C_{26}H_{52}B_3N_3$: C, 71.11; H, 11.94; N, 9.57. Found: C, 70.98; H, 11.90; N, 9.38.

[$Ph_2B(CH_2NMe_2)_2$][Li], [3][Li]: **2**[Li(TMEDA)$_2$] (1.0 g, 1.78 mmol) and 1,4-diazabicyclo[2,2,2]octane (DABCO) (5.0 g, 44.6 mmol) were dissolved in toluene (15 mL). The solution was heated in a 250 mL heavy-walled glass reaction vessel sealed with a Teflon cap to 100 ºC for 10 hours. The toluene was removed in vacuo and the remaining DABCO reagent was recovered via sublimation under static vacuum at 60 ºC. The DABCO·BH_3 complex was sublimed under dynamic vacuum at 125 ºC. The remaining white solid was washed with petroleum ether (2 x 2 mL) and dried in vacuo to afford analytically pure material (442 mg, 86%). ^1H NMR (acetone-d_6, 300 MHz): δ 7.31 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *ortho*-B(C_6H_5)$_2$), 6.98 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 6.80 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.81 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 2.47 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$. ^{13}C {^1H} NMR (acetone-d_6, 125.7 MHz): δ 162.4 (q, $^1J_{B-C}$ = 50.3 Hz, *ipso*-B(C_6H_5)$_2$), 133 (s, *ortho*-B(C_6H_5)$_2$), 127 (s, *meta*-B(C_6H_5)$_2$), 123 (s, *para*-B(C_6H_5)$_2$), 63.1 (q, $^1J_{B-C}$ = 43.4 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 47.7 (s, $Ph_2B(CH_2N(CH_3)_2)$. ^{11}B {^1H} NMR (acetone-d_6, 128.3 MHz): δ -17.8. ES-MS (Electrospray): calcd for $C_{18}H_{26}BN_2$ $(M)^-$ m/z 281, found $(M)^-$ m/z 281; $(M+2H)^+$ m/z 283, found 283. Anal. Calcd for $C_{18}H_{26}BLiN_2$: C, 75.02; H, 9.09; N, 9.72. Found: C, 74.89; H, 9.25 ; N, 9.75.

[$Ph_2B(CH_2NMe_2)_2$][H], [3][H]: [**2**][NEt_4] (261 mg, 0.6 mmol) and DABCO (3.33 g, 0.03 mol) were suspended in toluene (5 mL). The solution was heated to 100 ºC for 10 h in a vial capped with a Teflon cap. The toluene was removed in vacuo and the unused DABCO reagent was recovered via sublimation under vacuum at 60 ºC. [**3**][H] was precipitated from ethanol as a white solid, washed with petroleum ether (2 x 2 mL), and dried in vacuo to afford analytically pure material (78 mg, 47%). X-ray quality crystals were grown by slow evaporation of a benzene solution of [**3**][H]. ^1H NMR (acetone-d_6, 300 MHz): δ 7.31 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *ortho*-B(C_6H_5)$_2$), 6.98 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 6.80 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.81 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 2.47 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$. ^{11}B {^1H} NMR (acetone-d_6, 128.3 MHz): δ -24. ES-MS (Electrospray): calcd for $C_{18}H_{26}BN_2$ $(M)^-$ m/z 281, found $(M)^-$ m/z 281; $(M+2H)^+$ m/z 283, found 283.

$Ph_2B(CH_2NMe_2)_2Rh(NBD)$, 4: A solution of [**3**][Li] (50.2 mg, 0.17 mmol) in acetone (2 mL) was added to a solution of {(NBD)RhCl}$_2$ (40.2 mg, 0.17 mmol) in benzene (1 mL) at room temperature. After stirring for 2 h, the solvent was removed in vacuo to produce a yellow solid. The solids were dissolved in benzene and filtered through a Celite plug to remove LiCl salts. The benzene was removed in vacuo, and the solids were washed with petroleum ether (3 x 1.5 mL). Drying the solids in vacuo afforded analytically pure material (71.4 mg, 86%). X-ray quality crystals of **4** were grown by vapor diffusion of petroleum ether into benzene. ^1H NMR (C_6D_6, 300 MHz): δ 7.66 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.37 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.15 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 3.09 (b, 2H, NBD), 2.91 (dd, $^2J_{Rh-H}$ = 2.1, 5.1 Hz, 4H, NBD), 2.62 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 1.66 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$, 0.84 (b, 2H, NBD). ^{13}C {^1H} NMR (C_6D_6, 125.7 MHz): δ 165 (m, *ipso*-B(C_6H_5)$_2$), 133 (s, *ortho*-B(C_6H_5)$_2$), 128 (s, *meta*-B(C_6H_5)$_2$), 124 (s, *para* B(C_6H_5)$_2$), 65.2 (q, $^1J_{B-C}$ = 44.3 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 62.7 (NBD), 57.7 (d, $^1J_{Rh-C}$ = 10 Hz, NBD), 52.7 (s, $Ph_2B(CH_2N(CH_3)_2)$, 50.1 (NBD). ^{11}B {^1H} NMR (C_6D_6, 128.3 MHz): δ -17.5. ES-MS (Electrospray): calcd for $C_{25}H_{34}BN_2Rh$ $(M)^-$ m/z 476, found $(M)^+$ m/z 476. Anal. Calcd for $C_{25}H_{34}BN_2Rh$: C, 63.05; H, 7.20; N, 5.88. Found: C, 62.85; H, 7.18; N, 5.53.

$Ph_2B(CH_2NMe_2)_2Rh(CO)_2$, 5: A solution of {$(CO)_2RhCl$}$_2$ (30 mg, 0.077 mmol) in THF (0.5 mL) was added to a stirring solution of [**3**][Li] (44.4 mg, 0.154 mmol) in THF (1 mL) at room temperature. After stirring for 5 minutes, the yellow solution was filtered through a Celite plug to remove LiCl salts. The THF was removed in vacuo. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (60.3 mg, 89%). ^1H NMR (C_6D_6, 300 MHz): δ 7.66 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.37 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.15 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.66 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 1.73 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$. ^{13}C {^1H} NMR (C_6D_6, 125.7 MHz): δ 184, (bs, (*C*O)), 165 (m, *ipso*-B(C_6H_5)$_2$), 132.6 (s, *ortho*-B(C_6H_5)$_2$), 127.6 (s, *meta*-B(C_6H_5)$_2$), 123.5 (s, *para*-

B(C_6H_5)$_2$), 65.2 (q, $^1J_{B-C}$ = 44.3 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 52.7 (s, $Ph_2B(CH_2N(CH_3)_2)$. ^{11}B {^1H} NMR (C_6D_6, 128.3 MHz): δ -17.3. IR: (CH_2Cl_2, KBr) ν_{CO} = 2070, 1992 cm^{-1}. Anal. Calcd for $C_{20}H_{26}BN_2O_2Rh$: C, 54.58; H, 5.95; N, 6.36. Found: C, 54.16; H, 6.02; N, 6.34.

$Ph_2Si(CH_2N(CH_3)_2)_2$, 6: A solution of Ph_2SiCl_2 (0.86 g, 3.4 mmol) in toluene (2 mL) was added drop-wise to **1** (1.0 g, 6.6 mmol) in toluene (6 mL). The addition was complete after 5 min. The reaction was allowed to stir for 6 hours then the LiCl was removed via filtration through Celite on a sintered glass frit. Removal of toluene in vacuo afforded spectroscopically pure material (1.04 g, 95.5%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.75 (m, 4H, *ortho*-Si(C_6H_5)$_2$), 7.43 (m, 6H, H_{meta} and H_{para}-$SiPh_2$), 3.35 (s, 4H, $Ph_2Si(CH_2N(CH_3)_2)$, 2.41 (s, 12H, $Ph_2Si(CH_2N(CH_3)_2)$. ^{11}B {^1H} NMR ($CDCl_3$, 128.3 MHz): δ -6.9. ES-MS (Electrospray): calcd for $C_{18}H_{32}B_2N_2Si(M)^-$ m/z 326, found $(M+H)^-$ m/z 325, 311 (M-BH_3), 299 (M-2BH_3). Solid **6**·BH_3 (0.6 g, 1.84 mmol) and solid DABCO (4.5 g, 40.2 mmol) were suspended in toluene in a 250 mL heavy-walled glass reaction vessel sealed with a Teflon cap and heated to 110 ºC for 24 h. The toluene was removed in vacuo and the excess DABCO reagent was recovered by sublimation at 60 ºC. **6** was extracted into petroleum ether (3 x 5 mL) and yielded a white solid upon drying in vacuo (0.504g, 92%). ^1H NMR (C_6D_6, 300 MHz): δ 7.83 (m, 4H, *ortho*-Si(C_6H_5)$_2$), 7.22 (m, 6H, H_{meta} and H_{para}-$SiPh_2$), 2.51 (s, 4H, $Ph_2Si(CH_2N(CH_3)_2)$, 2.13 (s, 12H, $Ph_2Si(CH_2N(CH_3)_2)$. ^{13}C {^1H} NMR (C_6D_6, 125.7 MHz): δ 136.7 (s, *ipso*-Si(C_6H_5)$_2$), 136.2 (s, *ortho*-Si(C_6H_5)$_2$), 130 (s, *meta*-Si(C_6H_5)$_2$), 128.5 (s, *para*-Si(C_6H_5)$_2$), 50.5 (s, $Ph_2Si(CH_2N(CH_3)_2)$, 49.6 (s, $Ph_2Si(CH_2N(CH_3)_2)$. ES-MS (Electrospray): calcd for $C_{18}H_{32}N_2Si$ $(M)^-$ m/z 298, found $(M+H)^-$ m/z 299. Anal. Calcd for $C_{18}H_{26}N_2Si$: C, 72.43; H, 8.78; N, 9.38. Found: C, 72.70; H, 8.52; N, 9.17.

[{$Ph_2Si(CH_2N(CH_3)_2)_2$}$Rh(CO)_2$][PF_6], 7: A solution of {$(CO)_2RhCl$}$_2$ (20 mg, 0.051 mmol) in THF (0.5 mL) was added to a stirring solution of **6** (30.8 mg, 0.103 mmol) and $TlPF_6$ (36 mg, 0.103 mmol) in THF (1 mL) at room temperature. After stirring for 30 minutes, the yellow solution was filtered through a Celite plug to remove TlCl. The THF was removed in vacuo to afford analytically pure material (57 mg , 92%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.48 (m, 10H, Si(C_6H_5)$_2$), 2.89 (s, 4H, $Ph_2Si(CH_2N(CH_3)_2)$, 2.38 (s, 12H, $Ph_2Si(CH_2N(CH_3)_2)$. ^{13}C {^1H} NMR (C_6D_6, 125.7 MHz): δ 185 (bs, (*C*O)), 137.2 (s, *ipso*-Si(C_6H_5)$_2$), 136.7 (s, *ortho*-Si(C_6H_5)$_2$), 129.9 (s, *meta*-Si(C_6H_5)$_2$), 128.1 (s, *para*-Si(C_6H_5)$_2$), 50.8 (s, $Ph_2Si(CH_2N(CH_3)_2)$, 49.8 (s, $Ph_2Si(CH_2N(CH_3)_2)$. IR: (CH_2Cl_2, KBr) ν_{CO} = 2097, 2030 cm^{-1}. Anal. Calcd for $C_{20}H_{26}F_6N_2O_2PRhSi$: C, 39.88; H, 4.35; N, 4.65. Found: C, 39.52; H, 4.62; N, 4.68.

$Ph_2B(CH_2NMe_2)_2Rh(CO)(PMe_3)$, 8: PMe_3 (4.2 mg, 0.055 mmol) in THF (0.5 mL) was added drop-wise to a solution of **5** (23.8 mg, 0.054 mmol) in THF (1.5 mL). After stirring vigorously for 30 min the remaining solvent was removed in vacuo to produce an amber brown solid. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (19 mg, 76%). ^1H NMR (C_6D_6, 300 MHz): δ 7.89 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.68 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.16 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.70 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 2.65 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 1.71 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$, 1.68 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$, 1.15 (t, $^2J_{P-H}$ = 5.1 Hz, 9H, $P(CH_3)_3$). ^{31}P {^1H} NMR (C_6D_6, 121.4 MHz): δ 1.52 (d, $^1J_{Rh-P}$ = 128 Hz). ^{11}B {^1H} NMR (C_6D_6, 128.3 MHz): δ -16.2. IR: (CH_2Cl_2, KBr) ν_{CO} = 1972 cm^{-1}. Anal. Calcd for $C_{22}H_{35}BN_2OPRh$: C, 54.12; H, 7.23; N, 5.74. Found: C, 53.69; H, 7.39; N, 5.85.

$Ph_2B(CH_2NMe_2)_2Rh(CO)(PPh_3)$, 9: PPh_3 (13.5 mg, 0.052 mmol) in THF (1 mL) was added drop-wise to a solution of **5** (11.3 mg, 0.026 mmol) in THF (1.5 mL). After stirring vigorously for 30 min the remaining solvent was removed in vacuo to produce an amber solid. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (16.8 mg, 96%). ^1H NMR (C_6D_6, 300 MHz): δ 7.91 (m, 6H, *ortho*-P(C_6H_5)$_3$), 7.64 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.36 (t, $^3J_{H-H}$ = 6.3 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.15 (m, 2H, *para*-B(C_6H_5)$_2$), 7.01 (m, 9H, H_{meta} and H_{para}-PPh_3), 2.70 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 2.65 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 1.71 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$, 1.68 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$. ^{31}P {^1H} NMR (C_6D_6, 121.4 MHz): δ 30 (d, $^1J_{Rh-P}$ = 121 Hz). ^{11}B {^1H} NMR (C_6D_6, 128.3 MHz): δ -16.2. IR: (CH_2Cl_2, KBr) ν_{CO} = 1978 cm^{-1}. Anal. Calcd for $C_{37}H_{41}BN_2OPRh$: C, 65.89; H, 6.13; N, 4.15. Found: C, 65.55; H, 6.38; N, 4.22.

$Ph_2B(CH_2NMe_2)_2Rh(CO)$(1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene), 10: A solution of 2,6-diisopropylphenylimidazolylidene (50.2 mg, 0.128 mmol) was added dropwise to a solution of **5** (56.5 mg,

0.128 mmol) in THF (1.5 mL). After stirring vigorously for 1 h the remaining solvent was removed in vacuo to produce a brown solid. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (89 mg, 86%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.67 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.39 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.23 (m, 4H), 7.15 (m, 4H), 3.32 (s, 4H, ArN(CH_2)$_2$NAr), 3.24 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 2.72 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 2.68 (m, 2H, $Ph_2B(CH_2N(CH_3)_2)$, 1.71 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$, 1.69 (s, 6H, $Ph_2B(CH_2N(CH_3)_2)$, 1.26 (m, $^3J_{H-H}$ = 7.2 Hz, 24H, $CH(CH_3)_2$) . ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz): δ -16.8. IR: (CH_2Cl_2, KBr) ν_{CO} = 1948 cm^{-1}. Anal. Calcd for $C_{46}H_{66}BN_4ORh$: C, 68.65; H, 8.27; N, 6.96. Found: C, 68.19; H, 8.68; N, 7.08.

$Ph_2B(CH_2NMe_2)_2Rh(PMe_3)_2$, 11: PMe_3 (8 mg, 0.104 mmol) in benzene (0.5 mL) was added drop-wise to a solution of **4** (25 mg, 0.052 mmol) in benzene (1.5 mL). After stirring vigorously for 30 min the remaining solvent was removed in vacuo to produce a yellow solid. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (26 mg, 92%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.69 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.39 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.18 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.71 (m, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 1.76 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$, 1.16 (t, $^2J_{P-H}$ = 5.1 Hz, 9H, $P(CH_3)_3$). ^{13}C NMR {^{1}H} (C_6D_6, 125.7 MHz): δ 166 (m, *ipso*-B(C_6H_5)$_2$), 133 (s, *ortho*-B(C_6H_5)$_2$), 129 (s, *meta*-B(C_6H_5)$_2$), 123.5 (s, *para*-B(C_6H_5)$_2$), 65.2 (q, $^1J_{B-C}$ = 44.3 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 52.7 (s, $Ph_2B(CH_2N(CH_3)_2)$, 11.5 (t, $^1J_{P-C}$ = 12 Hz, $P(CH_3)_3$). ^{31}P {^{1}H} NMR (C_6D_6, 121.4 MHz): δ -15.8 (d, $^1J_{Rh-P}$ = 147 Hz). ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz): δ -17.0. Anal. Calcd for $C_{24}H_{44}BN_2P_2Rh$: C, 53.75; H, 8.27; N, 5.22. Found: C, 53.42; H, 8.44; N, 5.30.

$Ph_2B(CH_2NMe_2)_2Rh(NCCH_3)_2$, 12: Hydrogen (2.6 mL, 0.107 mmol) was syringed into a solution of **4** (25 mg, 0.053 mmol) in THF/ACN (1:1, 1.5 mL). After stirring vigorously for 1 hr, the solvent was removed in vacuo to produce a yellow solid. The solids were washed with petroleum ether and dried in vacuo to afford analytically pure material (23 mg, 92%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.67 (m, 4H, *ortho*-B(C_6H_5)$_2$), 7.39 (t, $^3J_{H-H}$ = 7.2 Hz, 4H, *meta*-B(C_6H_5)$_2$), 7.16 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *para*-B(C_6H_5)$_2$), 2.70 (q, $^2J_{B-H}$ = 3.6 Hz, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 1.71 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$, 1.37 (s, 6H, $(NCCH_3)$). ^{13}C {^{1}H} NMR (C_6D_6, 125.7 MHz): δ 165 (m, *ipso*-B(C_6H_5)$_2$), 132.6 (s, *ortho*-B(C_6H_5)$_2$), 127.6 (s, *meta* B(C_6H_5)$_2$), 123.5 (s, *para* B(C_6H_5)$_2$), 117 ($NCCH_3$), 65.2 (q, $^1J_{B-C}$ = 44.3 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 52.7 (s, $Ph_2B(CH_2N(CH_3)_2)$, 1.6 ($NCCH_3$). ^{11}B {^{1}H} NMR (C_6D_6, 128.3 MHz): δ -17.5. ES-MS (Electrospray): calcd for $C_{25}H_{34}BN_2Rh$ $(M)^-$ m/z 466, found $(M)^+$ m/z 425 (M-$NCCH_3$), 304 (M-2 $NCCH_3$). Anal. Calcd for $C_{22}H_{32}BN_4Rh$: C, 56.67; H, 6.92; N, 12.02. Found: (1) C, 54.15; H, 7.24; N, 12.24; (2) C, 53.98; H, 7.56; N, 12.38.

[{$Ph_2Si(CH_2N(CH_3)_2)_2$}Rh(NBD)][PF_6], 13: A solution of $[(NBD)RhCl]_2$ (20.2 mg, 0.043 mmol) in THF (1 mL) was added to a stirring solution of **6** (26 mg, 0.087 mmol) and $TlPF_6$ in THF (2 mL) at room temperature. After stirring for 2h, the TlCl was removed via filtration through a Celite plug whereupon the solvent was removed in vacuo. The solids were washed with petroleum ether (3 x 1.5 mL) and dried in vacuo to afford analytically pure material (26.4 mg, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (m, 10H, Si(C_6H_5)$_2$), 3.91 (s, 4H, NBD), 2.83 (s, 4H, $Ph_2Si(CH_2N(CH_3)_2)$, 2.33 (s, 12H, $Ph_2Si(CH_2N(CH_3)_2)$, 1.33 (s, 2H, NBD), 0.89 (bs, 2H, NBD). ^{13}C NMR {^{1}H}($CDCl_3$, 125.7 MHz): δ 136.6 (m, *ipso*-Si(C_6H_5)$_2$), 136.4 (s, *ortho*-Si(C_6H_5)$_2$), 130.0 (s, *meta*-Si(C_6H_5)$_2$), 128.5 (s, *para*-Si(C_6H_5)$_2$), 62.6 (NBD), 50.8 (s, $Ph_2Si(CH_2N(CH_3)_2)$, 57.4 (d, $^1J_{Rh-C}$ = 10 Hz, NBD), 50.1 (NBD), 49.9 (s, $Ph_2Si(CH_2N(CH_3)_2)$. Anal. Calcd for $C_{25}H_{34}F_6N_2PRhSi$: C, 47.03; H, 5.37; N, 4.39. Found: C, 46.99; H, 5.62; N, 4.18.

[$Ph_2B(CH_2NMe_2)_2$][NEt_4], 14: **Method A**: A solution of NEt_4Br (146 mg, 0.69 mmol) in EtOH (1 mL) was added to a suspension of [**3**][Li] (200 mg, 0.69 mmol) in EtOH (2 mL). The mixture was stirred vigorously and heated to 40 ºC for 7 days to complete the salt metathesis, which was judged complete by ^{1}H NMR. A stoichiometric equiv of LiBr was isolated. The EtOH solution was evaporated to dryness to leave a white solid. The solid was extracted into benzene and filtered through a Celite plug to remove LiCl salts. The solvent was removed in vacou to afford **14**. Given that this protocol required several days to go to completion, an alternative route to the target complex was preferred. **Method B**: $KOC(CH_3)_3$ (55 mg, 0.5 mmol) in 0.5 mL THF was added drop-wise to $[Ph_2B(CH_2NMe_2)_2][H]$ (100 mg, 0.25 mmol) in benzene (2 mL). $[Ph_2B(CH_2NMe_2)_2][K]$ precipitated from solution as a white solid that was isolated as follows (an analogous method using ^{t}BuLi or NaO^tBu affords $[Ph_2B(CH_2NMe_2)_2][Li]$ and $[Ph_2B(CH_2NMe_2)_2][Na]$, respectively): The supernatant was decanted and the remaining solids were then dried in vacuo. These

solids were subsequently washed with benzene (3 x 3mL) and petroleum ether (3 x 1.5 mL) and dried to afford pure $[Ph_2B(CH_2NMe_2)_2][K]$. The $[Ph_2B(CH_2NMe_2)_2][K]$ (25 mg, 0.078 mmol) was dissolved in ethanol (1.5 mL) and added to a solution of $[NEt_4][Br]$ (19.7 mg, 0.094 mmol) in ethanol (1 mL) and stirred for 4 h. Solid KBr precipitated from solution and was filtered over a sintered glass frit. The ethanol was removed in vacuo producing a white solid. The solids were washed with ethanol/petroleum ether (1:3, 3 mL) to afford analytically pure material **14** (29.6 mg, 92%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.33 (d, $^3J_{H-H}$ = 7.5 Hz, 4H, *ortho*-B(C_6H_5)$_2$), 6.92 (t, $^3J_{H-H}$ = 7.5 Hz, 4H, *meta*-B(C_6H_5)$_2$), 6.73 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, *para*-B(C_6H_5)$_2$), 3.42 (q, $^3J_{H-H}$ = 7.2 Hz, 8H, N(CH_2CH_3)$_4$), 2.57 (m, 4H, $Ph_2B(CH_2N(CH_3)_2)$, 2.22 (s, 12H, $Ph_2B(CH_2N(CH_3)_2)$, 3.42 (tt, $^3J_{H-H}$ = 2.1, 7.2 Hz, 12H, N(CH_2CH_3)$_4$). ^{13}C {^{1}H} NMR (acetone-d_6, 125.7 MHz, 25°C): δ 162.4 (q, $^1J_{B-C}$ = 50.3 Hz, *ipso*-B(C_6H_5)$_2$), 132.8 (s, *ortho*-B(C_6H_5)$_2$), 127 (s, *meta*-B(C_6H_5)$_2$), 123 (s, *para* B(C_6H_5)$_2$), 66 (bs, N(CH_2CH_3)$_4$), 63.1 (q, $^1J_{B-C}$ = 43.4 Hz, $Ph_2B(CH_2N(CH_3)_2)$, 47.7 (s, $Ph_2B(CH_2N(CH_3)_2)$, 23.8 (s, N(CH_2CH_3)$_4$). ^{11}B {^{1}H} NMR (acetone-d_6, 128.3 MHz, 25°C): δ -18.0. ES-MS (Electrospray): calcd for $C_{18}H_{26}BN_2$ $(M)^-$ m/z 281, found $(M)^-$ m/z 281; $(M+2H)^+$ m/z 283, found 283. Anal. Calcd for $C_{26}H_{46}BN_3$: C, 75.89; H, 11.27; N, 10.21. Found: C, 75.80; H, 11.43; N, 10.22.

Hydrogenation of styrene using 12: Complex **12** (1.0 mg, 0.0021 mmol) was dissolved in 100 μL of C_6D_6. Styrene (45.3 μL, 0.4 mmol) was diluted with 600 μL of acetone-d_6. 15 μL of the catalyst solution was added to the acetone solution of styrene. The combined solution was added to an NMR tube and sealed with a rubber septum. Hydrogen (1.0 mL, 0.5 mmol) was transferred via syringe into the NMR tube over a period of 5 minutes so as to allow the pressure to equalize by hydrogen dissolution. The NMR tube was shaken vigorously and the production of ethylbenzene was monitored via ^{1}H NMR. After 2.6 h, 50% of the styrene has been converted to ethylbenzene to provide a TOF of 188 mol product/ mol catalyst/ h.

Figure 1. Fully labeled drawing of $[Ph_2B(CH_2NMe_2)_2][H]$ [**3**][H]. Hydrogens have been omitted for clarity. The proton was found to have 80% population on N2 and 20% on N1 (shown localized on N2).

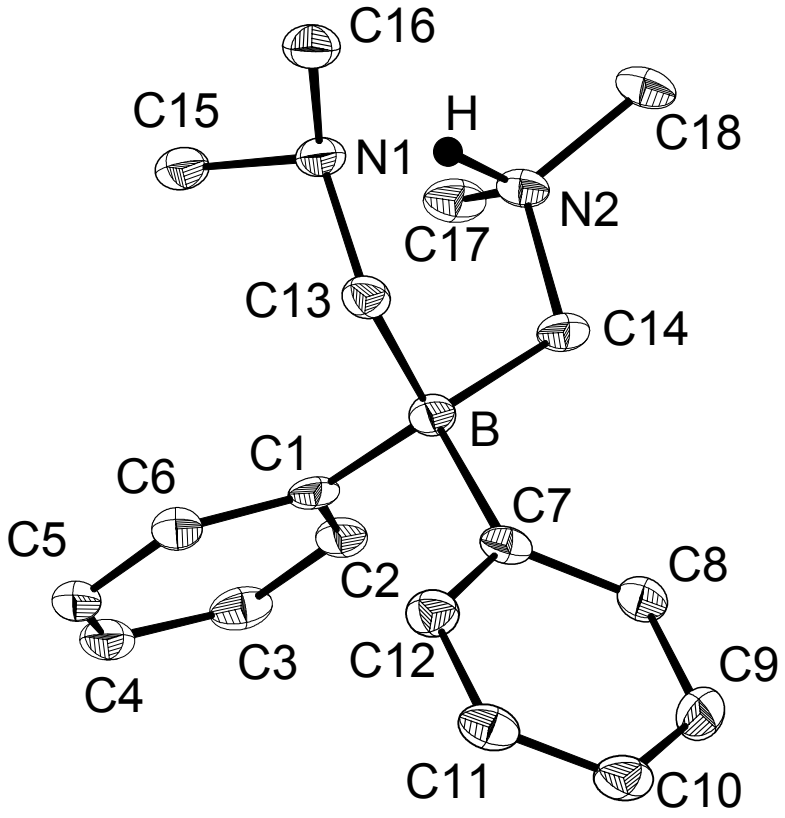

Figure 2. Fully labeled drawing of $Ph_2B(CH_2NMe_2)_2Rh(NBD)$ (**4**). Hydrogens have been omitted for clarity.

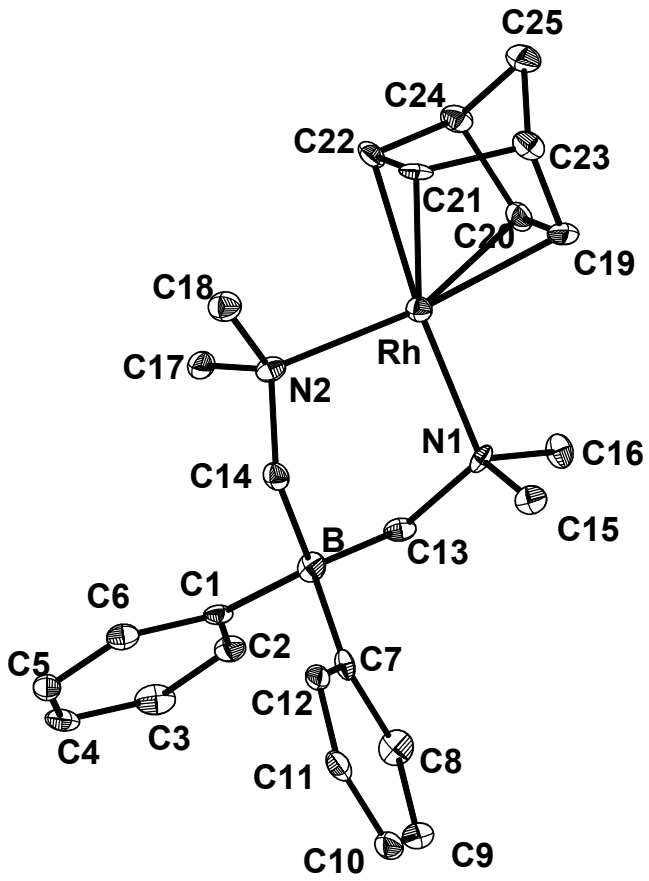

Table 1. Crystal data and structure refinement for $[Ph_2B(CH_2NMe_2)_2][H]$.

Identification code	tab10	
Empirical formula	$C_{18}H_{27}BN_2$	
Formula weight	282.23	
Temperature	96(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.7873(8) Å	α= 90°.
	b = 13.5711(14) Å	β= 91.467(2)°.
	c = 15.9311(17) Å	γ = 90°.
Volume	1685.8(3) $Å^3$	
Z	4	
Density (calculated)	1.112 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	616	
Crystal size	0.26 x 0.33 x 0.37 mm^3	
Theta range for data collection	1.97 to 28.92°.	
Index ranges	-10<=h<=10, -18<=k<=17, -20<=l<=21	
Reflections collected	25880	
Independent reflections	4145 [R(int) = 0.1383]	
Completeness to theta = 28.92°	93.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4145 / 0 / 198	
Goodness-of-fit on F^2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.0855, wR2 = 0.1115	
R indices (all data)	R1 = 0.0978, wR2 = 0.1184	
Largest diff. peak and hole	0.367 and -0.278 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Ph_2B(CH_2NMe_2)_2][H]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7457(2)	8419(1)	1082(1)	20(1)
N(2)	7951(2)	6546(1)	619(1)	20(1)
B	4913(2)	7108(1)	1187(1)	19(1)
C(1)	3714(2)	7313(1)	342(1)	19(1)
C(2)	3420(2)	6621(1)	-289(1)	21(1)
C(3)	2347(2)	6794(1)	-988(1)	24(1)
C(4)	1496(2)	7681(1)	-1070(1)	24(1)
C(5)	1712(2)	8377(1)	-448(1)	23(1)
C(6)	2802(2)	8200(1)	238(1)	21(1)
C(7)	3581(2)	6729(1)	1902(1)	19(1)
C(8)	3437(2)	5751(1)	2152(1)	25(1)
C(9)	2247(2)	5441(1)	2735(1)	31(1)
C(10)	1159(2)	6109(1)	3095(1)	27(1)
C(11)	1266(2)	7083(1)	2872(1)	25(1)
C(12)	2455(2)	7378(1)	2287(1)	23(1)
C(13)	5945(2)	8084(1)	1561(1)	20(1)
C(14)	6375(2)	6237(1)	1088(1)	20(1)
C(15)	6929(2)	8963(1)	327(1)	24(1)
C(16)	8596(2)	9037(1)	1601(1)	26(1)
C(17)	7707(2)	6462(1)	-299(1)	26(1)
C(18)	9518(2)	6007(1)	901(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for $[Ph_2B(CH_2NMe_2)_2][H]$.

N(1)-C(16)	1.463(2)	C(17)-N(2)-C(14)	112.58(12)
N(1)-C(15)	1.463(2)	C(18)-N(2)-C(14)	112.63(13)
N(1)-C(13)	1.4912(19)	C(1)-B-C(7)	105.41(12)
N(2)-C(17)	1.475(2)	C(1)-B-C(14)	115.03(14)
N(2)-C(18)	1.483(2)	C(7)-B-C(14)	106.93(12)
N(2)-C(14)	1.5134(19)	C(1)-B-C(13)	114.89(13)
B-C(1)	1.643(2)	C(7)-B-C(13)	108.01(13)
B-C(7)	1.645(2)	C(14)-B-C(13)	106.14(12)
B-C(14)	1.652(2)	C(2)-C(1)-C(6)	114.75(15)
B-C(13)	1.653(2)	C(2)-C(1)-B	123.89(14)
C(1)-C(2)	1.392(2)	C(6)-C(1)-B	121.22(14)
C(1)-C(6)	1.405(2)	C(1)-C(2)-C(3)	123.23(15)
C(2)-C(3)	1.395(2)	C(4)-C(3)-C(2)	119.98(15)
C(3)-C(4)	1.379(2)	C(5)-C(4)-C(3)	118.76(16)
C(4)-C(5)	1.378(2)	C(4)-C(5)-C(6)	120.58(15)
C(5)-C(6)	1.388(2)	C(5)-C(6)-C(1)	122.67(15)
C(7)-C(8)	1.391(2)	C(8)-C(7)-C(12)	114.90(14)
C(7)-C(12)	1.396(2)	C(8)-C(7)-B	123.57(14)
C(8)-C(9)	1.395(2)	C(12)-C(7)-B	121.49(14)
C(9)-C(10)	1.376(2)	C(7)-C(8)-C(9)	122.52(15)
C(10)-C(11)	1.373(2)	C(10)-C(9)-C(8)	120.46(16)
C(11)-C(12)	1.390(2)	C(11)-C(10)-C(9)	118.96(16)
C(16)-N(1)-C(15)	109.24(12)	C(10)-C(11)-C(12)	119.80(15)
C(16)-N(1)-C(13)	111.19(13)	C(11)-C(12)-C(7)	123.35(15)
C(15)-N(1)-C(13)	111.53(12)	N(1)-C(13)-B	116.25(12)
C(17)-N(2)-C(18)	110.31(13)	N(2)-C(14)-B	114.72(12)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Ph_2B(CH_2NMe_2)_2][H]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	15(1)	23(1)	22(1)	1(1)	2(1)	-3(1)
N(2)	13(1)	25(1)	23(1)	-2(1)	4(1)	0(1)
B	16(1)	22(1)	19(1)	2(1)	4(1)	0(1)
C(1)	12(1)	24(1)	20(1)	1(1)	7(1)	-4(1)
C(2)	14(1)	25(1)	22(1)	1(1)	6(1)	0(1)
C(3)	21(1)	33(1)	18(1)	-3(1)	6(1)	-8(1)
C(4)	16(1)	36(1)	20(1)	7(1)	0(1)	-4(1)
C(5)	15(1)	26(1)	28(1)	5(1)	3(1)	0(1)
C(6)	17(1)	23(1)	21(1)	0(1)	3(1)	-1(1)
C(7)	13(1)	26(1)	17(1)	-2(1)	-2(1)	-1(1)
C(8)	16(1)	27(1)	31(1)	4(1)	6(1)	5(1)
C(9)	26(1)	30(1)	36(1)	14(1)	9(1)	2(1)
C(10)	18(1)	42(1)	22(1)	6(1)	5(1)	-2(1)
C(11)	17(1)	35(1)	22(1)	-5(1)	4(1)	2(1)
C(12)	20(1)	24(1)	25(1)	-2(1)	4(1)	0(1)
C(13)	16(1)	24(1)	19(1)	1(1)	3(1)	2(1)
C(14)	15(1)	25(1)	20(1)	0(1)	5(1)	-3(1)
C(15)	18(1)	29(1)	26(1)	4(1)	3(1)	-4(1)
C(16)	19(1)	30(1)	29(1)	0(1)	-1(1)	-5(1)
C(17)	18(1)	37(1)	24(1)	-1(1)	8(1)	-2(1)
C(18)	13(1)	32(1)	30(1)	-5(1)	3(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Ph_2B(CH_2NMe_2)_2][H]$.

	x	y	z	U(eq)
H(2)	3977	6000	-242	25
H(3)	2203	6301	-1407	29
H(4)	775	7809	-1547	29
H(5)	1109	8984	-488	27
H(6)	2938	8698	653	25
H(8)	4178	5276	1915	30
H(9)	2188	4765	2885	37
H(10)	346	5898	3491	33
H(11)	530	7555	3117	30
H(12)	2503	8056	2141	28
H(13A)	5120	8637	1588	23
H(13B)	6337	7937	2143	23
H(14A)	6742	6011	1655	24
H(14B)	5839	5669	793	24
H(15A)	6317	9562	486	37
H(15B)	6171	8549	-24	37
H(15C)	7947	9142	12	37
H(16A)	9594	9230	1277	39
H(16B)	8982	8667	2099	39
H(16C)	7977	9628	1774	39
H(17A)	8723	6719	-575	39
H(17B)	6695	6842	-480	39
H(17C)	7542	5768	-452	39
H(18A)	9362	5301	797	38
H(18B)	9723	6119	1502	38
H(18C)	10504	6246	590	38
H	8060(20)	7279(13)	772(11)	28(5)

Table 6. Crystal data and structure refinement for $\{Ph_2B(CH_2NMe_2)_2\}Rh(NBD)$.

Identification code	tab14	
Empirical formula	$C_{25}H_{34}BN_2Rh$	
Formula weight	476.26	
Temperature	96(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.2330(11) Å	α= 90°.
	b = 9.5382(9) Å	β= 91.504(2)°.
	c = 18.5995(17) Å	γ = 90°.
Volume	2169.5(3) $Å^3$	
Z	4	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.801 mm^{-1}	
F(000)	992	
Crystal size	0.04 x 0.10 x 0.20 mm^3	
Theta range for data collection	1.97 to 28.43°.	
Index ranges	-15<=h<=15, -12<=k<=12, -24<=l<=24	
Reflections collected	31607	
Independent reflections	5160 [R(int) = 0.1057]	
Completeness to theta = 28.43°	94.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5160 / 0 / 266	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.0621	
R indices (all data)	R1 = 0.0811, wR2 = 0.0671	
Largest diff. peak and hole	1.508 and -0.669 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $\{Ph_2B(CH_2NMe_2)_2\}Rh(NBD)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh	7495(1)	10365(1)	-254(1)	11(1)
N(1)	8022(2)	8185(3)	-326(1)	11(1)
N(2)	6961(2)	10160(3)	849(1)	13(1)
B	7470(3)	7421(4)	1017(2)	14(1)
C(1)	6419(3)	6611(3)	1361(2)	12(1)
C(2)	5808(3)	5579(3)	993(2)	16(1)
C(3)	5013(3)	4781(4)	1309(2)	19(1)
C(4)	4784(3)	4974(3)	2026(2)	17(1)
C(5)	5359(3)	5985(3)	2409(2)	15(1)
C(6)	6149(3)	6768(3)	2083(2)	14(1)
C(7)	8508(3)	6569(3)	1382(2)	11(1)
C(8)	8745(3)	5199(4)	1168(2)	18(1)
C(9)	9540(3)	4385(4)	1498(2)	18(1)
C(10)	10147(3)	4908(3)	2071(2)	17(1)
C(11)	9943(3)	6253(4)	2299(2)	16(1)
C(12)	9141(3)	7061(3)	1960(2)	13(1)
C(13)	7365(3)	7247(3)	142(2)	12(1)
C(14)	7587(3)	9062(3)	1263(2)	13(1)
C(15)	9186(3)	8118(3)	-112(2)	16(1)
C(16)	7917(3)	7661(4)	-1070(2)	16(1)
C(17)	5792(3)	9831(3)	855(2)	15(1)
C(18)	7116(3)	11501(3)	1243(2)	17(1)
C(19)	8335(3)	11056(3)	-1179(2)	16(1)
C(20)	7251(3)	10797(3)	-1371(2)	15(1)
C(21)	7758(3)	12553(3)	-278(2)	14(1)
C(22)	6680(3)	12301(3)	-461(2)	15(1)
C(23)	8389(3)	12605(3)	-971(2)	15(1)
C(24)	6625(3)	12166(3)	-1276(2)	16(1)
C(25)	7512(3)	13224(3)	-1487(2)	20(1)

Table 8. Bond lengths [Å] and angles [°] for $\{Ph_2B(CH_2NMe_2)_2\}Rh(NBD)$.

Rh-C(21)	2.112(3)	C(19)-C(20)	1.385(5)
Rh-C(22)	2.129(3)	C(19)-C(23)	1.529(4)
Rh-C(20)	2.130(3)	C(19)-H(19)	0.9500
Rh-C(19)	2.132(3)	C(20)-C(24)	1.527(4)
Rh-N(2)	2.179(3)	C(20)-H(20)	0.9500
Rh-N(1)	2.182(3)	C(21)-C(22)	1.373(5)
N(1)-C(15)	1.470(4)	C(21)-C(23)	1.520(4)
N(1)-C(16)	1.473(4)	C(21)-H(21)	0.9500
N(1)-C(13)	1.497(4)	C(22)-C(24)	1.522(4)
N(2)-C(17)	1.463(4)	C(22)-H(22)	0.9500
N(2)-C(18)	1.484(4)	C(23)-C(25)	1.538(4)
N(2)-C(14)	1.499(4)	C(23)-H(23)	1.0000
B-C(14)	1.636(5)	C(24)-C(25)	1.541(4)
B-C(13)	1.639(5)	C(24)-H(24)	1.0000
B-C(7)	1.640(5)	C(25)-H(25A)	0.9900
B-C(1)	1.643(5)	C(25)-H(25B)	0.9900
C(1)-C(6)	1.400(4)	C(21)-Rh-C(22)	37.79(12)
C(1)-C(2)	1.404(4)	C(21)-Rh-C(20)	78.81(13)
C(2)-C(3)	1.379(4)	C(22)-Rh-C(20)	66.65(13)
C(2)-H(2)	0.9500	C(21)-Rh-C(19)	66.47(13)
C(3)-C(4)	1.382(4)	C(22)-Rh-C(19)	79.60(13)
C(3)-H(3)	0.9500	C(20)-Rh-C(19)	37.94(12)
C(4)-C(5)	1.381(4)	C(21)-Rh-N(2)	99.10(12)
C(4)-H(4)	0.9500	C(22)-Rh-N(2)	95.58(12)
C(5)-C(6)	1.375(4)	C(20)-Rh-N(2)	153.87(11)
C(5)-H(5)	0.9500	C(19)-Rh-N(2)	161.98(12)
C(6)-H(6)	0.9500	C(21)-Rh-N(1)	153.48(11)
C(7)-C(12)	1.390(4)	C(22)-Rh-N(1)	162.42(11)
C(7)-C(8)	1.399(4)	C(20)-Rh-N(1)	99.11(11)
C(8)-C(9)	1.377(4)	C(19)-Rh-N(1)	95.47(12)
C(8)-H(8)	0.9500	N(2)-Rh-N(1)	93.94(10)
C(9)-C(10)	1.375(5)	C(15)-N(1)-C(16)	107.4(2)
C(9)-H(9)	0.9500	C(15)-N(1)-C(13)	110.3(2)
C(10)-C(11)	1.376(4)	C(16)-N(1)-C(13)	107.9(3)
C(10)-H(10)	0.9500	C(15)-N(1)-Rh	108.08(19)
C(11)-C(12)	1.385(4)	C(16)-N(1)-Rh	111.3(2)
C(11)-H(11)	0.9500	C(13)-N(1)-Rh	111.71(19)
C(12)-H(12)	0.9500	C(17)-N(2)-C(18)	107.1(2)
C(13)-H(13A)	0.9900	C(17)-N(2)-C(14)	109.4(2)
C(13)-H(13B)	0.9900	C(18)-N(2)-C(14)	107.0(2)
C(14)-H(14A)	0.9900	C(17)-N(2)-Rh	110.09(19)
C(14)-H(14B)	0.9900	C(18)-N(2)-Rh	110.5(2)
C(15)-H(15A)	0.9800	C(14)-N(2)-Rh	112.6(2)
C(15)-H(15B)	0.9800	C(14)-B-C(13)	112.2(3)
C(15)-H(15C)	0.9800	C(14)-B-C(7)	107.3(3)
C(16)-H(16A)	0.9800	C(13)-B-C(7)	113.7(3)
C(16)-H(16B)	0.9800	C(14)-B-C(1)	113.9(3)
C(16)-H(16C)	0.9800	C(13)-B-C(1)	107.3(3)
C(17)-H(17A)	0.9800	C(7)-B-C(1)	102.2(3)
C(17)-H(17B)	0.9800	C(6)-C(1)-C(2)	114.0(3)
C(17)-H(17C)	0.9800	C(6)-C(1)-B	122.0(3)
C(18)-H(18A)	0.9800	C(2)-C(1)-B	123.5(3)
C(18)-H(18B)	0.9800	C(3)-C(2)-C(1)	123.5(3)
C(18)-H(18C)	0.9800	C(3)-C(2)-H(2)	118.2

C(1)-C(2)-H(2)	118.2	N(2)-C(17)-H(17A)	109.5
C(2)-C(3)-C(4)	120.1(3)	N(2)-C(17)-H(17B)	109.5
C(2)-C(3)-H(3)	120.0	H(17A)-C(17)-H(17B)	109.5
C(4)-C(3)-H(3)	120.0	N(2)-C(17)-H(17C)	109.5
C(5)-C(4)-C(3)	118.5(3)	H(17A)-C(17)-H(17C)	109.5
C(5)-C(4)-H(4)	120.7	H(17B)-C(17)-H(17C)	109.5
C(3)-C(4)-H(4)	120.7	N(2)-C(18)-H(18A)	109.5
C(6)-C(5)-C(4)	120.5(3)	N(2)-C(18)-H(18B)	109.5
C(6)-C(5)-H(5)	119.8	H(18A)-C(18)-H(18B)	109.5
C(4)-C(5)-H(5)	119.8	N(2)-C(18)-H(18C)	109.5
C(5)-C(6)-C(1)	123.4(3)	H(18A)-C(18)-H(18C)	109.5
C(5)-C(6)-H(6)	118.3	H(18B)-C(18)-H(18C)	109.5
C(1)-C(6)-H(6)	118.3	C(20)-C(19)-C(23)	105.8(3)
C(12)-C(7)-C(8)	114.9(3)	C(20)-C(19)-Rh	70.97(19)
C(12)-C(7)-B	124.2(3)	C(23)-C(19)-Rh	96.5(2)
C(8)-C(7)-B	120.6(3)	C(20)-C(19)-H(19)	127.1
C(9)-C(8)-C(7)	123.3(3)	C(23)-C(19)-H(19)	127.1
C(9)-C(8)-H(8)	118.3	Rh-C(19)-H(19)	100.2
C(7)-C(8)-H(8)	118.3	C(19)-C(20)-C(24)	107.3(3)
C(10)-C(9)-C(8)	120.1(3)	C(19)-C(20)-Rh	71.10(19)
C(10)-C(9)-H(9)	120.0	C(24)-C(20)-Rh	96.4(2)
C(8)-C(9)-H(9)	120.0	C(19)-C(20)-H(20)	126.3
C(9)-C(10)-C(11)	118.6(3)	C(24)-C(20)-H(20)	126.3
C(9)-C(10)-H(10)	120.7	Rh-C(20)-H(20)	100.3
C(11)-C(10)-H(10)	120.7	C(22)-C(21)-C(23)	107.5(3)
C(10)-C(11)-C(12)	120.7(3)	C(22)-C(21)-Rh	71.74(19)
C(10)-C(11)-H(11)	119.6	C(23)-C(21)-Rh	97.5(2)
C(12)-C(11)-H(11)	119.6	C(22)-C(21)-H(21)	126.2
C(11)-C(12)-C(7)	122.4(3)	C(23)-C(21)-H(21)	126.2
C(11)-C(12)-H(12)	118.8	Rh-C(21)-H(21)	98.9
C(7)-C(12)-H(12)	118.8	C(21)-C(22)-C(24)	106.2(3)
N(1)-C(13)-B	119.2(3)	C(21)-C(22)-Rh	70.47(19)
N(1)-C(13)-H(13A)	107.5	C(24)-C(22)-Rh	96.6(2)
B-C(13)-H(13A)	107.5	C(21)-C(22)-H(22)	126.9
N(1)-C(13)-H(13B)	107.5	C(24)-C(22)-H(22)	126.9
B-C(13)-H(13B)	107.5	Rh-C(22)-H(22)	100.5
H(13A)-C(13)-H(13B)	107.0	C(21)-C(23)-C(19)	99.4(3)
N(2)-C(14)-B	119.0(3)	C(21)-C(23)-C(25)	100.4(3)
N(2)-C(14)-H(14A)	107.6	C(19)-C(23)-C(25)	100.8(3)
B-C(14)-H(14A)	107.6	C(21)-C(23)-H(23)	117.6
N(2)-C(14)-H(14B)	107.6	C(19)-C(23)-H(23)	117.6
B-C(14)-H(14B)	107.6	C(25)-C(23)-H(23)	117.6
H(14A)-C(14)-H(14B)	107.0	C(22)-C(24)-C(20)	100.2(3)
N(1)-C(15)-H(15A)	109.5	C(22)-C(24)-C(25)	100.7(3)
N(1)-C(15)-H(15B)	109.5	C(20)-C(24)-C(25)	99.9(3)
H(15A)-C(15)-H(15B)	109.5	C(22)-C(24)-H(24)	117.6
N(1)-C(15)-H(15C)	109.5	C(20)-C(24)-H(24)	117.6
H(15A)-C(15)-H(15C)	109.5	C(25)-C(24)-H(24)	117.6
H(15B)-C(15)-H(15C)	109.5	C(23)-C(25)-C(24)	94.2(3)
N(1)-C(16)-H(16A)	109.5	C(23)-C(25)-H(25A)	112.9
N(1)-C(16)-H(16B)	109.5	C(24)-C(25)-H(25A)	112.9
H(16A)-C(16)-H(16B)	109.5	C(23)-C(25)-H(25B)	112.9
N(1)-C(16)-H(16C)	109.5	C(24)-C(25)-H(25B)	112.9
H(16A)-C(16)-H(16C)	109.5	H(25A)-C(25)-H(25B)	110.3
H(16B)-C(16)-H(16C)	109.5		

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\{Ph_2B(CH_2NMe_2)_2\}Rh(NBD)$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh	12(1)	11(1)	10(1)	0(1)	-1(1)	0(1)
N(1)	10(2)	13(2)	10(2)	-5(1)	-1(1)	5(1)
N(2)	12(2)	11(2)	15(2)	-1(1)	-3(1)	1(1)
B	16(2)	16(2)	9(2)	-3(2)	-2(2)	2(2)
C(1)	10(2)	10(2)	15(2)	4(2)	-3(2)	2(2)
C(2)	15(2)	15(2)	17(2)	3(2)	-1(2)	3(2)
C(3)	17(2)	13(2)	25(2)	-1(2)	-7(2)	-5(2)
C(4)	11(2)	15(2)	26(2)	11(2)	1(2)	1(2)
C(5)	14(2)	19(2)	12(2)	4(2)	0(2)	6(2)
C(6)	12(2)	15(2)	16(2)	2(2)	-5(2)	2(2)
C(7)	9(2)	15(2)	10(2)	0(2)	3(2)	-4(2)
C(8)	18(2)	22(2)	14(2)	-5(2)	-6(2)	0(2)
C(9)	22(2)	13(2)	19(2)	2(2)	3(2)	4(2)
C(10)	15(2)	20(2)	15(2)	6(2)	2(2)	4(2)
C(11)	15(2)	21(2)	12(2)	5(2)	3(2)	-1(2)
C(12)	16(2)	9(2)	13(2)	0(2)	4(2)	-1(2)
C(13)	12(2)	8(2)	16(2)	0(2)	-4(2)	-1(2)
C(14)	12(2)	17(2)	9(2)	2(2)	-1(2)	1(2)
C(15)	16(2)	15(2)	16(2)	-1(2)	-2(2)	1(2)
C(16)	18(2)	20(2)	8(2)	-3(2)	0(2)	-2(2)
C(17)	12(2)	14(2)	18(2)	1(2)	2(1)	1(2)
C(18)	20(2)	15(2)	17(2)	-1(2)	-1(2)	0(2)
C(19)	20(2)	13(2)	15(2)	5(2)	0(2)	6(2)
C(20)	17(2)	18(2)	9(2)	3(2)	1(2)	1(2)
C(21)	16(2)	8(2)	17(2)	6(2)	-4(2)	1(2)
C(22)	25(2)	10(2)	12(2)	2(2)	6(2)	-3(2)
C(23)	11(2)	19(2)	14(2)	5(2)	-4(2)	-2(2)
C(24)	15(2)	17(2)	15(2)	4(2)	-2(2)	0(2)
C(25)	23(2)	14(2)	24(2)	6(2)	4(2)	-1(2)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\{Ph_2B(CH_2NMe_2)_2\}Rh(NBD)$.

	x	y	z	U(eq)
H(2)	5951	5421	500	19
H(3)	4622	4098	1034	22
H(4)	4242	4424	2250	21
H(5)	5208	6140	2901	18
H(6)	6532	7451	2363	17
H(8)	8337	4811	775	22
H(9)	9670	3460	1331	22
H(10)	10695	4352	2304	20
H(11)	10356	6631	2692	19
H(12)	9020	7987	2130	15
H(13A)	7559	6267	24	15
H(13B)	6585	7374	1	15
H(14A)	7371	9126	1771	15
H(14B)	8372	9312	1250	15
H(15A)	9437	7144	-131	23
H(15B)	9285	8477	379	23
H(15C)	9612	8690	-441	23
H(16A)	8325	8275	-1389	23
H(16B)	7144	7651	-1222	23
H(16C)	8213	6708	-1093	23
H(17A)	5650	8980	572	22
H(17B)	5374	10613	646	22
H(17C)	5571	9678	1351	22
H(18A)	6704	12245	994	26
H(18B)	7895	11744	1261	26
H(18C)	6853	11400	1733	26
H(19)	8923	10405	-1178	19
H(20)	6954	9928	-1531	18
H(21)	8055	12673	195	16
H(22)	6089	12227	-142	19
H(23)	9124	13064	-954	18
H(24)	5890	12249	-1521	19
H(25A)	7710	13149	-1999	24
H(25B)	7321	14204	-1369	24